Cooperative Research in C1 Chemistry

Six month report on research conducted from
May 1, 2001 to October 31, 2001
DOE Contract No. DE-FC26-99FT40540

Prepared by the Consortium for Fossil Fuel Science

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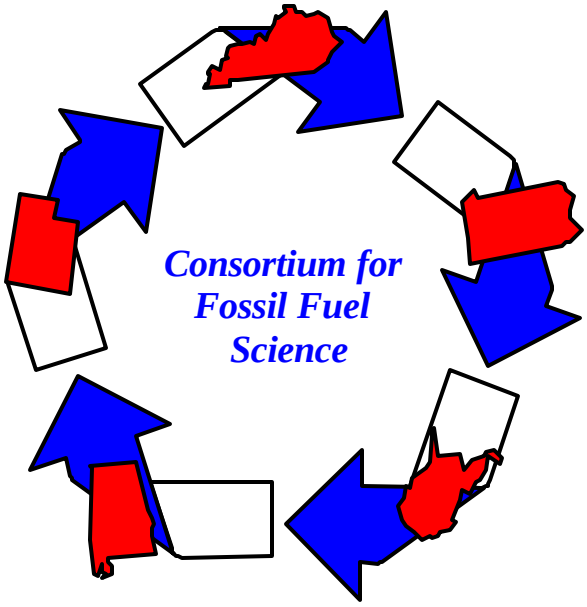

University of Kentucky *West Virginia University* *University of Pittsburgh*

University of Utah *Auburn University*

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I. Background

Faculty and students from five universities (Kentucky, West Virginia, Utah, Pittsburgh and Auburn) are collaborating on a basic research program to develop novel C1 chemistry processes for the production of clean, high quality transportation fuel. An Industrial Advisory Board (IAB) with members from Chevron, Eastman Chemical, Energy International, the Department of Defense, and Teir Associates has been formed to provide practical guidance to the program. The program has two principal objectives.

1. Develop technology for conversion of C1 source materials (natural gas, synthesis gas, carbon dioxide and monoxide, and methanol) into clean, high efficiency transportation fuel.
2. Develop novel processes for producing hydrogen from natural gas, synthesis gas, and other hydrocarbons.

The current report summarizes progress made towards these goals during the first six months of the third year of the program (FY 2001). The report is divided into three sections: Fuels and Chemicals, Hydrogen, and Advanced Characterization and Testing.

II. Fuels and Chemicals

Effect of Probe Molecules on Oxygenated Products in Fischer-Tropsch Synthesis (Y. Zhang, J.W. Tierney, and I. Wender, University of Pittsburgh)

It is reported that particulate matter emission (PME) reduction of 4-10% can be achieved for every 1% of oxygen blended into diesel fuel. We are investigating the production of oxygenated diesel fuels by modifying Fischer-Tropsch (F-T) catalysts and reaction conditions, and by hydroformylation of high olefinic F-T products. The addition of acetylenic molecules, specifically 1- and 2-hexyne into the F-T synthesis with iron and cobalt catalysts to produce oxygenated products appears to be a promising approach.

1-Hexyne is readily incorporated into the F-T reaction to produce heptanol, heptanal and C8+ straight chain alcohols. In the case of 2-hexyne addition, a large amount of branched C7+ oxygenates are produced. At lower temperatures, these hexynes initiate chain-growth in the F-T reaction and produce mainly C7+ products. The mode of incorporation of acetylenic molecules into F-T reactions is under investigation.

Supercritical Fluids as an Alternate Reaction Medium for Fischer-Tropsch Synthesis (Xiwen Huang, Yoonkook Park, Christine W. Curtis, and Christopher B. Roberts, Auburn University)

Supercritical fluids (SCFs) offer several advantages over traditional solvents as reaction media for catalytic reactions including the ability to manipulate the reaction environment through simple changes in pressure to enhance solubility of reactants and products, to eliminate interphase transport limitations, and to integrate reaction and separation unit operations. Advantages of SCF-phase Fischer-Tropsch synthesis (SCF-FT) include gaslike diffusivities and liquid-like solubilities, which together combine the desirable features of the gas- and liquid-phase FT synthesis routes. These advantages can be attributed to the SCF offering high diffusivities and improved heat transfer (relative to a liquid) and high solubility (relative to a gas).

We have investigated FT synthesis under SCF hexane conditions in a continuous, high-pressure reactor by employing traditional Fe and Co catalysts (e.g. 15%Co-0.5Pd-Al_2O_3). Steady state operation was quickly achieved under SCF conditions and the overall product distributions obtained were quite constant over extended periods of operation (over 40 hours). The SCF-FT process has a marked effect on the hydrocarbon product distribution with a shift to higher carbon number products owing to enhanced heat and mass transfer from the catalyst surface. Relatively flat product distributions with similar mass percentages of the C11-C17 products were obtained. In addition, an obvious difference in the olefin content is observed, as the 1-olefin content in the SCF phase is always higher than in gas- or liquid-phase. This phenomenon suggests that the SCF-FT reaction rate in not diffusion controlled, whereas the secondary olefin hydrogenation and isomerization reactions are diffusion limited. The SCF-FT process results in higher diffusitivity and more rapid removal of high molecular weight 1-olefins from the catalyst surface thereby suppressing secondary hydrogenation and isomerization reactions.

Diethyl Carbonate: An Oxygenated Automotive Fuel Additive (Brian Dunn, N. S. Roh, Guojin Wang, Stephen Hilton, Edward M. Eyring, Ronald J. Pugmire, and Henk L.C. Meuzelaar, University of Utah)

Diethyl carbonate (DEC) is a molecule with more oxygen per mole than other molecules such as MTBE and ethanol that are used as automotive fuel additives. Experiments in a test diesel engine have confirmed that DEC is effective at diminishing exhaust particulates. Synthesis of DEC from CO, O_2, and ethanol has a maximum product yield of 20% at 150°C using a Cu/Pd/activated carbon catalyst pretreated with potassium hydroxide. Evidence suggests that a combination of two copper salts is required for effective catalysis of the DEC synthesis.

Alternative Synthetic Schemes for the Catalytic Production of Diethyl Carbonate (Brian C. Dunn, Thomas A. Cutler, Emily Heider, and Edward M. Eyring, University of Utah)

A new class of heterogeneous catalysts for the synthesis of diethyl carbonate (DEC) has been developed. The catalysts are based on metal ions (Cu^{2+} and Pd^{2+}) coordinated to a silica framework by chloride or amine pendant functionality. The catalysts are prepared via a sol-gel route using 3-aminopropyl-triethoxysilane or 3-chloropropyl-trimethoxysilane combined with traditional sol-gel precursors such as tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS). Three different methods of preparation have been attempted: 1) combining a complex between the metal ions and the derivatized silanes with TEOS or TMOS before gelation; 2) initially creating the derivatized silica framework, then coordinating the metal ions to the pendant amino or chloro sites; and 3) using a complex between the metal ions and the chloro or amino silanes to attach to an existing silica framework via condensation reactions. Performance of catalysts prepared by these three methods is under investigation.

In electrified micro heterogeneous catalysis ("EMC," Rolison and Stemple, 1994), zeolite Y particles are impregnated with appropriate catalytic metals, and a suspension of these particles in water at ~1°C is maintained between closely spaced (0.4 cm) low DC voltage platinum electrodes by an upward flow of reactant gases. When palladium (II) and copper(II) are the metals on the surface of sodium zeolite Y particles, a gas mixture of propene and oxygen is converted to propylene oxide rather than acetone with a selectivity of 76%. Recent experiments at Utah aimed at synthesizing diethyl carbonate from CO, O_2, and ethanol by the EMC method will be described.

Hydroisomerization and Hydrocracking of Fischer-Tropsch Waxes (Z. Zhou, Y. Zhang, L. Lou, J.W. Tierney, and I. Wender, University of Pittsburgh)

Work on the conversion of long chain normal paraffins produced in the Fischer-Tropsch synthesis to high quality gasoline, diesel fuel and lube-base oils at mid reaction conditions by hydroisomerization and hydrocracking using platinum-promoted tungsten-modified zirconia catalysts is ongoing. In a current study, platinum promoted zeolites are being used as hydroisomerization and hydrocracking catalysts. By varying the balance between metallic and acidic functions, differences in catalytic activity and product distributions are being investigated.

Production of Ethylene, Propylene and Light Hydrocarbons via C-1 Chemistry (James A. Guin, Shaobin Wang, and Delphine Dubois, Auburn University)

The conversion of syngas and/or methanol to light olefins and hydrocarbons by new and effective molecular sieve catalysts is being studied. We are beginning with the modification of silicoaluminophosphates (SAPO's) by optimizing the catalyst preparation and composition via characterization/testing and optimization of reaction conditions. We have constructed a continuous quartz tube flow reactor for testing of catalysts and have developed the necessary analytical methodology for gas phase analysis. Several different molecular sieve catalysts effective for formation of light olefins, especially ethylene and propylene, have been prepared and tested.

Production of High-Molecular-Weight Alcohols and Other Oxygenates from Synthesis Gas Using a Promoted Molybdenum-On-Carbon Catalyst (Lawrence Norcio, Edwin L. Kugler, and Dady B. Dadyburjor, West Virginia University)

Carbon-supported molybdenum-based catalysts, promoted with Ni and K, were found to be good catalysts for higher-alcohol synthesis. Reactivity studies were carried out in a computer-controlled reactor system, modified to allow for collection of liquid products. Vapor-phase products were also analyzed. The reactor was run isothermally at 250, 300, and 350°C. At low severities, the liquid product contains appreciable quantities of C_{1-5} alcohols in an aqueous phase with no hydrocarbon phase. When the liquid product is injected into a simulated-distillation column, alcohols up to C_{24} are shown to be present. At more severe conditions, other oxygenates are also formed, and a two-phase liquid product is obtained. Only small quantities of methane and traces of ethane and propane are found in the vapor phase. The calculated selectivity to higher alcohols (wt.% CO_2-free) at T=350°C is 61%. The carbon mass-balance measurements obtained were very good, 98 percent or better.

III. Hydrogen

Production of Hydrogen and Carbon Nanotubes by Catalytic Decomposition of Methane (Naresh Shah, Devadas Panjala, and Gerald P. Huffman, University of Kentucky)

Traditionally, hydrogen has been produced by reforming or partial oxidation of methane to produce synthesis gas, followed by the water-gas shift reaction to convert CO to CO_2 and produce more hydrogen, followed in turn by a purification or separation procedure. We are investigating the direct catalytic decomposition of undiluted methane into pure hydrogen and carbon using nanoscale, binary, Fe-M catalysts (M = Pd, Mo, and Ni) supported on alumina [(4.5% Fe – 0.5%M)/Al_2O_3]. All of the supported Fe-M catalysts reduced the methane decomposition temperature by 400-500 °C relative to non-catalytic thermal decomposition and exhibited significantly higher activity than Fe or any of the secondary metals (Pd, Mo, and Ni) supported on alumina alone. At reaction temperatures of approximately 700-800°C and space velocities of 0.1/hr, the product stream was comprised of over 85-volume % of hydrogen, with the balance being unconverted methane. No C2 or higher hydrocarbons were observed in the product gas. High resolution SEM and TEM characterization indicated that almost all carbon produced at 700°C is in the form of potentially useful multi-walled nanotubes. At higher temperatures (>900°C), hydrogen production is substantially decreased and carbon is deposited on the catalysts in the form of amorphous carbon, carbon flakes, and carbon fibers. In the non-catalytic, thermal decomposition mode at temperatures above 900°C, graphitic carbon film is deposited everywhere in the reactor. Thus, the morphology of the carbon produced may be the controlling parameter in the catalytic decomposition of methane. The efficient removal of the carbon from the catalyst surface in the form of nanotubes may be the key factor influencing catalyst performance.

Dry Reforming of Methane using a Cobalt-Tungsten Carbide Catalyst (Mahesh Iyer, Lawrence Norcio, Dady B. Dadyburjor and Edwin L. Kugler, West Virginia University)

For the dry reforming of methane with carbon dioxide, carbide catalysts seem to be stable without any significant formation of coke. A preliminary investigation of the performance of the cobalt-tungsten carbide catalyst, Co_6W_6C, is presented. An unsupported Co_6W_6C catalyst with a particle size of less than 38 microns was tested for activity at various reaction temperatures and feed ratios in a stainless steel differential reactor. The catalyst was found to be very stable for over 72 hours and gave stable CH_4 and CO_2 conversions of 17% and 23% respectively, at 850°C with a feed ratio of $CH_4/CO_2 = 1$. The catalyst was tested for activity at different partial pressures of CH_4 and CO_2 at 775 and 750°C, which show the effects on the reaction rates of methane reforming (r_{MR}), reverse water gas shift (r_{RW}), and carbon deposition (r_{CD}) reactions. Future research will focus on reforming with steam, steam-carbon dioxide mixtures, and the water-gas shift reaction.

IV. Advanced Characterization and Testing

Investigations of Copper Chloride and Tungstated Zirconia Catalysts using X-ray Diffraction and Electron Spin Resonance Spectroscopy (Alex Punnoose and M.S. Seehra, West Virginia University)

CuCl2/PdCl2/activated carbon catalysts are being used for the synthesis of diethyl carbonate (Eyring et al) and Pt/WOx/ZrO2 catalysts are being used for the synthesis of high octane-index gasoline components (Wender et al). In our work, we have employed electron spin resonance (ESR) and x-ray diffraction (XRD) to determine the nature of the active species in these reactions, by comparing the catalytic activity with the observed species in XRD and ESR. For Pt/WOx/ZrO2, we observe ESR signals that suggest electron transfer between W5+ and Zr3+ states. For the synthesis of diethyl carbonate, evidence points to paratacamite being the active species. Details of these results will soon be published.

Molecular Structure of Binary Methane Decomposition Catalysts (Frank E. Huggins, Naresh Shah, Sidhartha Pattanaik, Panjala Devadas, and Gerald P. Huffman, University of Kentucky)

Nanoscale, binary Fe-M catalysts supported on alumina (M = Mo, Pd, Ni) exhibit high activity for the catalytic decomposition of methane into hydrogen and carbon nanotubes. In order to better understand the catalytic reaction mechanisms, the molecular structure of the catalysts is being investigated by x-ray absorption fine structure (XAFS) spectroscopy and Mössbauer spectroscopy. Additionally, a high temperature in situ XAFS cell has been constructed to permit investigation of catalyst structure at temperature under reaction conditions. Several conclusions of this work are presented. First, in order for the catalyst to be active, it must be at least partially in the metallic state. This has been confirmed by both in situ XAFS measurements at 700°C and by ex situ Mössbauer and XAFS measurements at room temperature on previously reduced and reacted catalysts. Second, the spectroscopy data indicates the Mo, Pd, and Ni are all

incorporated into an alloy phase with the Fe. In the case of the Mo, a specific intermetallic compound, Fe_2Mo was identified.

Effects of Oxygenated Fuel Additives on Diesel Engine Emissions (Jacek P. Dworzanski, Guojin Wang, David Wagner, Brian Dunn, Ronald J. Pugmire, Edward M. Eyring, Neil S. Arnold and Henk L.C. Meuzelaar, University of Utah)

Emissions from a diesel test engine using conventional diesel blended with diethyl carbonate or ethanol additives were monitored using instruments for on-line measurement of volatile organic compounds (VOC) and particulate matter (PM). A variety of load conditions were used to simulate "real world" emission scenarios, while marker compounds were used to examine lubricant contributions to emission profiles. Reduced formation of PM has been observed for oxygenated fuels, along with variations in VOC and PM emission profiles under varying conditions.

NMR Characterization of Particulates from Diesel Engine Tests and Insights into the Reaction Mechanisms for Formation of Diethyl Carbonate (Ronald J. Pugmire, Mark S. Solum, Brian H. Dunn, Edward M. Eyring, Guojin Wang, N.S. Rho, and Kerry Kelley, University of Utah)

The Utah team has focused on two major objectives: 1) synthesis of diethylcarbonate as a fuel additive and 2) obtaining fuel additive performance data in a diesel engine. Synthesis methods have been developed and tested in a batch reactor and a flow reactor. Diethylcarbonate is the primary product in the synthesis scheme but the product distribution seems to vary between the batch and flow reactor processes. ^{13}C labeled starting materials ($^{13}CH_3DH_2OH$, CH_3 $^{13}CH_2OH$, and ^{13}CO) were used to identify reaction products adsorbed on the catalyst surface and suggest possible reaction pathways for isotope incorporation in the two different processes. NMR and ESR data were obtained on particulate samples collected from diesel engine tests (at idle and under load) of a standard fuel with and without diethylcarbonate additive.